

THE INTERCALATION ISOTHERM OF FERRIC CHLORIDE VAPOR ON GRAPHITE FROM 300 TO 350°C*

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Abstract—The isotherm of ferric chloride vapor on graphite was determined in a vacuum system with a recording spring balance in the range 300° to 350°C. For natural graphite there was a very low threshold pressure for intercalation, two pressure independent compositions of C_7FeCl_3 and $C_{12}FeCl_3$ (350° only), hysteresis and a dilute residue "compound". The two compositions were obtained at room temperature by air cooling and found to be stable in hydrochloric acid. The C_7FeCl_3 decomposed in vacuum at 275°C to C_7FeCl_2 and Cl_2 . Exposure of the C_7FeCl_3 to 60 cm Cl_2 at 350°C removed all the iron as the volatile $FeCl_3$. For pyrolytic graphite the threshold pressure was much higher, there were no pressure independent compositions and the saturated vapor at 300°C gave $C_{10}FeCl_3$. There was hysteresis on desorption and a dilute residue compound.

1. INTRODUCTION

FERRIC chloride was first shown to react with graphite by THIELE.⁽¹⁾ A detailed study by RUDORFF and SCHULZ⁽²⁾ claimed that two compounds are formed: $C_{10}FeCl_3$ between 180° and 309°C and $C_{30}FeCl_3$ between 310° and 410°C both after acid washing. In an X-ray and electron diffraction study, COWLEY and IBERS⁽³⁾ showed that a $C_{12}FeCl_3$ was 17% free graphite. Radioactive iron has been used⁽⁴⁾ to show a lack of exchange between a $C_{12}FeCl_3$ and ferric ion in solution. All of these workers heated graphite with anhydrous $FeCl_3$ in a bomb at temperatures above 180°C followed by air cooling and washing with HCl solution. The final composition may therefore have been different from the equilibrium composition at high temperature. Our purpose was to remove this possibility by determining the isotherm of ferric chloride vapor on graphite. In addition, the threshold pressure for intercalation, any hysteresis and the residue composition could all be measured for the first time.

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2. EXPERIMENTAL

Dry Cl_2 was passed over hot 99.85% iron wire and the ferric chloride was distilled in a stream of Cl_2 into an ampoule which was then evacuated to 10^{-5} cm and sealed. The ampoule was transferred to the side arm (Fig. 1) of an all glass helical spring balance which used a high temperature differential transformer to follow the weight of the graphite sample hung from the silica spring. The furnaces were added, the cross tube was sealed in place, the system was evacuated to 10^{-5} cm and sealed. The ampoule was then magnetically broken. The electronic details and operation of a similar room temperature balance have been described.⁽⁵⁾ Pressure was measured optically with a Pyrex spiral gauge in an envelope at a measured pressure—sensitivity 1 cm of scale per cm of Hg. Two furnaces controlled to 0.5°C maintained the spring, gauge and sample at one temperature and the ampoule at a lower temperature. Heating tape controlled the cross tube temperature.

The transformer height could be changed in the hot furnace by the three screws A. The other three screws B allowed adjustment to a horizontal position before the furnace was lowered. Sensitivity

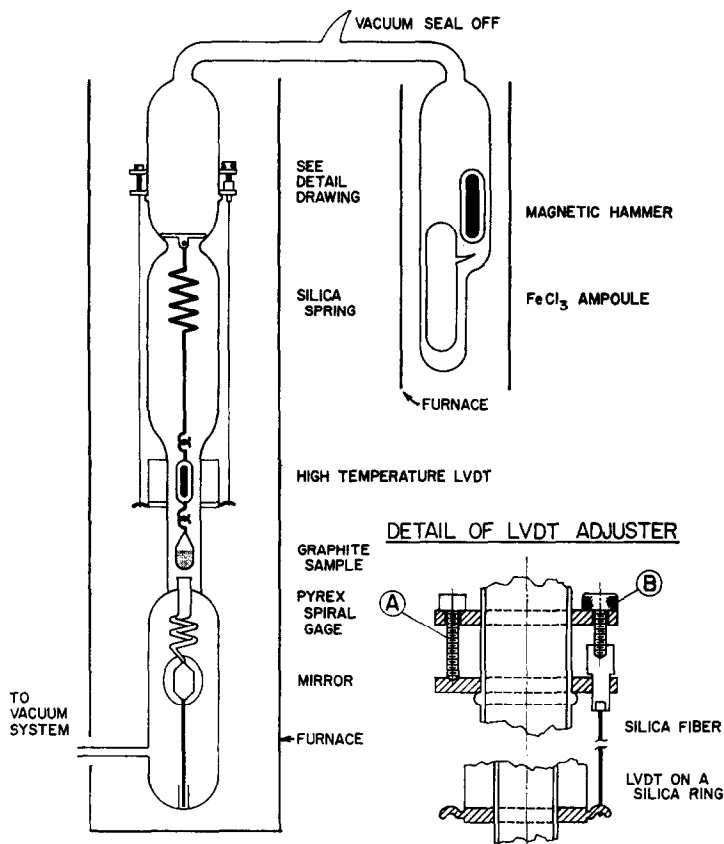


FIG. 1. Recording balance and pressure gauge 20–350°C.

was measured at each temperature used by removing the pressure gauge and placing known weights in a bucket suspended from the transformer core and far below it. The value was about 1 mV per mg over a range of 300 mV. All temperatures were measured with iron–constantan couples said to be within 0.3 per cent of the N.B.S. Fahrenheit temperature. The buoyancy correction was determined with ferric chloride vapor to be 0.1 mg per cm of Hg in the range 300–350°C.

3. RESULTS

Compositions are referred to as mole ratios using the nearest whole number of carbon atoms to one FeCl_3 molecule. This is not to suggest that these are actual compounds.

Natural graphite

The material was Spectroscopic Carbon SP1

from the National Carbon Co. used in previous work.⁽⁶⁾ The isotherm at 300°C from zero pressure to saturation is shown in Fig. 2. At each pressure it was found that 24 hr was sufficient to reach a weight constant to 1 per cent. Note that the threshold pressure was below the gauge sensitivity of 0.25 cm Hg, that C_7FeCl_3 is the only pressure independent composition observed, that there was hysteresis and that the final residue was $\text{C}_{22}\text{FeCl}_3$. Before the balance was opened, the isotherm was repeated. The threshold pressure was again too low to measure, the absorption curve led smoothly into the previous one and the desorption curve was duplicated. Finally, a fresh sample of SP-1 gave exactly the same isotherm.

Because an earlier report⁽²⁾ claimed that only $\text{C}_{30}\text{FeCl}_3$ is formed above 309°C, an isotherm was run at 310°C. It resembled Fig. 2 displaced along

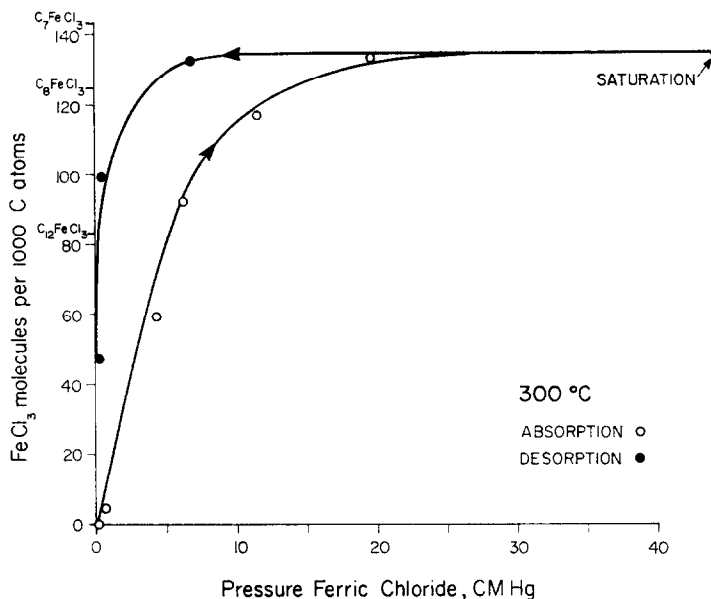


FIG. 2. Isotherm of ferric chloride on natural graphite 300°C.

the pressure axis. The threshold pressure was measurable this time and was 0.75 cm Hg. The only pressure independent composition was C_7FeCl_3 from 25 cm to saturation at 65 cm Hg. The residue was $C_{33}FeCl_3$.

The isotherm at 350°C is shown in Fig. 3. The threshold pressure is now 1.5 cm Hg and C_7FeCl_3 is still a pressure independent composition. However, a new composition of $C_{12}FeCl_3$ appears during absorption. On desorption $C_{10}FeCl_3$ may be formed in the range 12–8 cm Hg and the final residue is $C_{50}FeCl_3$. A second run on this residue confirmed the $C_{12}FeCl_3$ plateau.

From the absorption curves at 300°, 310° and 350°C an Arrhenius plot was made for each of the compositions 20, 40 and 60 $FeCl_3$ per 1000 C atoms. The three slopes gave an isosteric heat of 13.0 ± 1.0 kcal per mole with no trend with composition.

Synthetic graphite

A pyrolytic graphite from High Temperature Labs in Boston was used. It was polynucleated at 2150°C, had a density of 2.21 g cm^{-3} and was used as 10 discs each 0.26 cm dia. $\times$ 0.10 cm thick. It was designated PGI in previous work with Br_2 .⁽⁷⁾ At 300°C the threshold pressure was 15 cm Hg

after which the composition rose steadily to $C_{12}FeCl_3$ at the saturation pressure of 45 cm Hg. On desorption the composition increased to about $C_{10}FeCl_3$ and fell to $C_{30}FeCl_3$ below 2 cm Hg. This increase is believed to be the result of not waiting long enough at saturation to reach equilibrium. Pyrolytic graphite splits into thin flakes on intercalation and previous work⁽⁷⁾ has shown this to be a slow process.

A significant feature of all the runs with natural and synthetic graphite was that the pressure in the system fell to zero when the temperature was finally reduced to 20°C. There was also no evidence for the production of any $FeCl_2$ residue in the balance system. This means that the iron in the graphite residue is there as $FeCl_3$ and $2FeCl_2 + Cl_2$ or either one of these two entities.

Bomb preparations

The purpose was to obtain C_7 and $C_{12}FeCl_3$ at room temperature using conditions based on the above isotherms. An inverted glass U-tube containing SP1 in one arm and iron wire in the other was evacuated to 10^{-5} cm and then opened to dry Cl_2 at 1 atm. Gentle heating of the iron gave $FeCl_3$ with no appreciable loss from the U-tube. Overheating gave some $FeCl_2$ but this readily formed

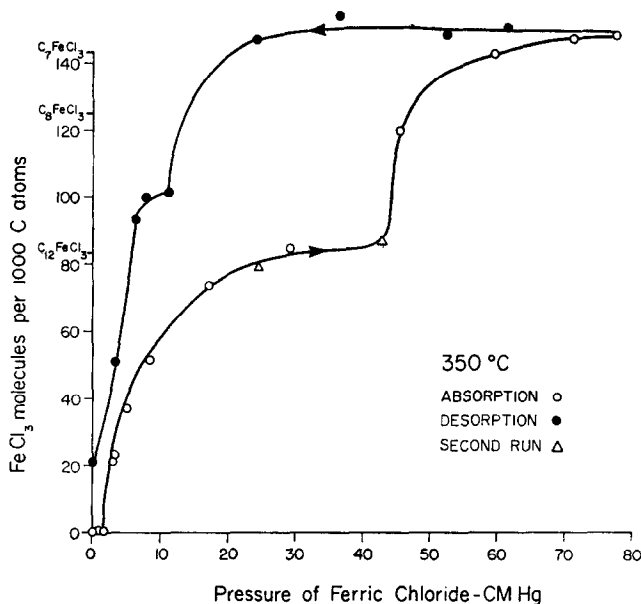


FIG. 3. Isotherm of ferric chloride on natural graphite
350°C.

FeCl_3 on cooling. When conversion was complete the cold system was evacuated and sealed. This reproduces the initial conditions in the balance.

C_7FeCl_3

When both arms were held at 300°C for 24 hr before cooling, the product was C_7FeCl_3 after washing with hot 6 M HCl. The 002 and 004 lines of graphite were absent from the X-ray pattern of this product. ASHER and WILSON⁽⁸⁾ have stated that 5% graphite is the minimum content to show these lines. Further extraction with 6 M HCl in a Soxhlet removed less than 1 mg from 700 mg in 24 hr. The product was analyzed by complete combustion in an oxygen flask and titration of the solution with an Aminco-Cotlove Chloride Titrator, 42.7% found, 43.0% theory. The possibility that slower cooling of the U-tube might trap less FeCl_3 was checked by cooling at 10° per hr. The acid washed product was again C_7FeCl_3 .

The thermal decomposition of C_7FeCl_3 was studied by heating it in a vacuum of 10^{-5} cm Hg while continuously following the weight with a recording balance.⁽⁵⁾ The minimum temperature required for noticeable weight loss was 275°C. Above this, appreciable amounts of FeCl_3 condensed above the furnace. At 275°C, however, less

than 1% was lost in this way as shown by collecting the sublimate and titrating for chloride. After 4 days the weight was constant and corresponded to complete conversion to $2\text{FeCl}_2 + \text{Cl}_2$. The Cl_2 produced was continuously condensed in a trap. The product was 33.2% Cl whereas C_7FeCl_2 is 33.5% Cl. This was extracted to constant weight with hot 6 M HCl and lost 25 per cent of its FeCl_2 content. In another run the C_7FeCl_2 residue was exposed to 65 cm of Cl_2 gas. There was no noticeable weight change below 300°C. Above this however, the weight decreased and ferric chloride condensed above the furnace. The final weight was that of the graphite in the original C_7FeCl_3 .

$\text{C}_{12}\text{FeCl}_3$

When the graphite in the U-tube was held at 350°C and the FeCl_3 arm at 295°C for 24 hr before air cooling, the product was $\text{C}_{12.4}\text{FeCl}_3$ after washing. This was expected because at 295°C the vapor pressure of FeCl_3 is 30 cm Hg which is the middle of the $\text{C}_{12}\text{FeCl}_3$ plateau in the isotherm.

Stainless steel bomb runs

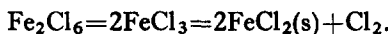
Some workers have used steel bombs especially above 310°C where the FeCl_3 pressure is 1 atm.

The effect of this on the composition was studied by loading a 304 stainless steel bomb with SP1 graphite and anhydrous ferric chloride in a dry N₂ glove box. After 24 hr at 300°C it was cooled at 10°C per hr in one run and chilled in cold water in a second. Both acid washed products were C₁₂FeCl₃ which is the approximate composition reported by some previous workers.^(2,4,9) When the quantities were increased so that the graphite powder was 5 mm deep instead of 1 mm, final compositions of C₂₀₋₃₀FeCl₃ were obtained after 24 hr at 300°C. Finally, a stainless steel bar was placed in the glass tube before the vacuum preparation of C₇FeCl₃ in a U-tube was carried out. The product was C₉FeCl₃ and the bar had lost weight.

4. DISCUSSION

Threshold pressure

The P_t for intercalation of natural graphite by FeCl₃ is about 0.01 relative to saturation at 310°C and 0.003 at 350°C. These are not known accurately enough to compare or to discuss especially in view of the fact that the vapor is an equilibrium mixture:



At 300°C it is mostly Fe₂Cl₆ with 3 cm Cl₂ at saturation. However, the P_t is low compared with those for ICl (0.03), Br₂ (0.05) and CrO₂Cl₂ (0.4) all at 20°C. This order is related neither to molecular size nor to dipole moment.

The high P_t of 0.3 for PG1 is in agreement with previous work^(7,10) with Br₂. The high P_t in pyrolytic graphite was believed to be associated with the greater amount of interlayer bonding. There is, however, a curious fact. For FeCl₃ the ratio of the threshold pressures of PG1 to SP1 at 310°C is 30. For Br₂ the same ratio at 20°C is 5. A possible reason for this difference appears if we consider P_t to arise from two factors: (1) The ease of transfer of electrons to the FeCl₃ or Br₂; and (2) The rigidity of the layer system. Now the first should increase with temperature because this will increase the population of the conduction band and make electrons more available for transfer. The second factor will not be sensitive to temperature until the interlayer bonds arising from non aligned layers can be annealed out and this occurs only above about 2500°C. Hence in the 20–350°C range the P_t of a graphite with relatively few inter-

layer bonds such as SP1 should be more sensitive to temperature than a graphite such as PG1 where interlayer bonding is the major factor in determining P_t . Hence the ratio of P_t for PG1 to SP1 should increase with temperature as observed.

Adsorption heats

The intercalation part of the isotherm^(6,11) gives the following isosteric heats in kcal/mole in natural graphite—FeCl₃ 13, ICl 12, Br₂ 12 and CrO₂Cl₂ 13. It is interesting that these are all low and about the same. The process to which they refer is unknown because there is hysteresis and one cannot be sure that the solid phase is homogeneous or of the same structure for the same composition at different temperatures.

Structure and composition

There are two pressure independent compositions C₇FeCl₃ at both 300° and 350°C and C₁₂-FeCl₃ at 350°C. The latter may have been missed at 300° and 310° because of the narrow relative pressure range over which it is stable. This range would be about 1 cm Hg at 300°C whereas it is 20 cm at 350°C. The inflexion near C₁₀FeCl₃ on desorption at 350°C is not well defined. It may be C₁₂FeCl₃ plus the residue composition.

Ferric chloride is a layer structure consisting of a hexagonal network of Fe atoms 3.5 Å apart with a hexagonal network of Cl atoms both above and below. If one such triple layer occupies every layer space in graphite and has the same Fe atom separation as in solid ferric chloride then one obtains C_{6.1}FeCl₃. If alternate spaces are occupied then it is C_{12.2}FeCl₃. Now to be exact we observed in the vapor C_{6.7-7.2}FeCl₃ and C_{12.0}FeCl₃ and in the preparations from the chilled vapor C_{7.1} and C_{12.4}. Two of these agree well with the stage 2 compound postulated above. The others are higher in carbon than the postulated C_{6.1}FeCl₃. They do, however, agree with the results of COWLEY and IBERS⁽³⁾ who reported their 55.5 per cent composition C_{10.9}FeCl₃ to contain 17 per cent free graphite by X-ray measurements. They noted that this was equivalent to a compound of 66.9 per cent FeCl₃ or C_{6.7}FeCl₃ as compared with C_{6.1}FeCl₃ for one with completely filled layers. Our preparations from the vapor may contain some free graphite formed during cooling by escape of FeCl₃ from the peripheral area of each crystal. The collapse of these areas to the normal

graphite spacing traps the remaining FeCl_3 and accounts for the stability in 6 M HCl. The amount is less than 5 per cent as shown by the absence of the 002 and 004 lines of graphite.⁽⁸⁾ Our compositions quoted above do show a loss of FeCl_3 in going from the vapor to the solid. They give 0.7 and 1.5 per cent free graphite in the solid stage 1 and 2 compounds respectively. However, these are not precise values.

Others have obtained a variety of compositions all with less FeCl_3 than in our C_7FeCl_3 . There are three possibilities. One applies to preparation in steel bombs. In FeCl_3 vapor there is an equilibrium:



Presumably this equilibrium also exists in the C_7FeCl_3 solid at 300–350°C. Furthermore between the gas phase and the solid C_7FeCl_3 the FeCl_3 would be in equilibrium and also the Cl_2 . Now in a steel bomb Cl_2 would be removed from the gas phase to form iron chloride. This would shift the above equilibrium to the right in both the gas phase and in the graphite. Hence the FeCl_3 pressure may fall below that required to produce C_7FeCl_3 . Furthermore the loss of Cl_2 from the solid would decrease the total weight of adduct and lead to higher calculated ratios of carbon to ferric chloride. A second factor in air or N_2 loaded bombs is the depth of graphite. As this increases the time required for the vapor to diffuse throughout the graphite should increase. Hence the uptake in a given time may decrease. We did observe this in two runs. Finally, particle size may be a factor in determining the amount of FeCl_3 lost in cooling the bomb. Small crystals should trap less adduct.

Thermal decomposition of C_7FeCl_3

The data shows that the amount of FeCl_3 sublimed is negligible at 275°C but increases for higher temperatures. The remainder is converted to FeCl_2 and Cl_2 which escapes. The FeCl_2 can then be completely removed by exposure to 60 cm Cl_2 at 350°C. This could be a peripheral attack to form FeCl_3 which sublims out of the layer spaces leaving a path for Cl_2 to attack the exposed FeCl_2 and so on to the centre of the crystal.

Residue "Compounds"

These are somewhat more concentrated than for

Br_2 but different rates of pressure reduction may account for this. The apparent decrease of FeCl_3 content at higher temperature may again be a pressure reduction effect or a result of the greater mobility of FeCl_3 at the higher temperature.

5. CONCLUSIONS

The intercalation of natural graphite by FeCl_3 vapor at 350°C resembles that by ICl at 20°C in that there is a low threshold pressure and two pressure independent compositions— C_{12} and C_7FeCl_3 . At 300°C only the latter was detected. On desorption there is hysteresis and a residue whose composition is of the same order of magnitude as for Br_2 . The above two compositions were obtained from the equilibrium mixture with FeCl_3 vapor by air cooling and were both stable in hot 6 M HCl probably because of a peripheral region of graphite around each flake. The two compositions may be stage 1 and 2 compounds in which graphite spaces are filled or nearly filled by FeCl_3 layers having the same structure as in FeCl_3 solid. The slow thermal decomposition of C_7FeCl_3 produces C_7FeCl_2 and Cl_2 . The reaction is reversible although under the conditions used the FeCl_3 formed in the graphite sublimed leaving pure graphite. The high threshold pressure of FeCl_3 in pyrolytic graphite relative to natural graphite has been related to the population of the conduction band and interlayer bonding. The variety of reported compositions for graphite ferric chloride may be a combination of lack of equilibrium, presence of steel and a possible effect of particle size.

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